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Cetylpyridinium Chloride - A Versatile Reagent for Precipitation Titrations

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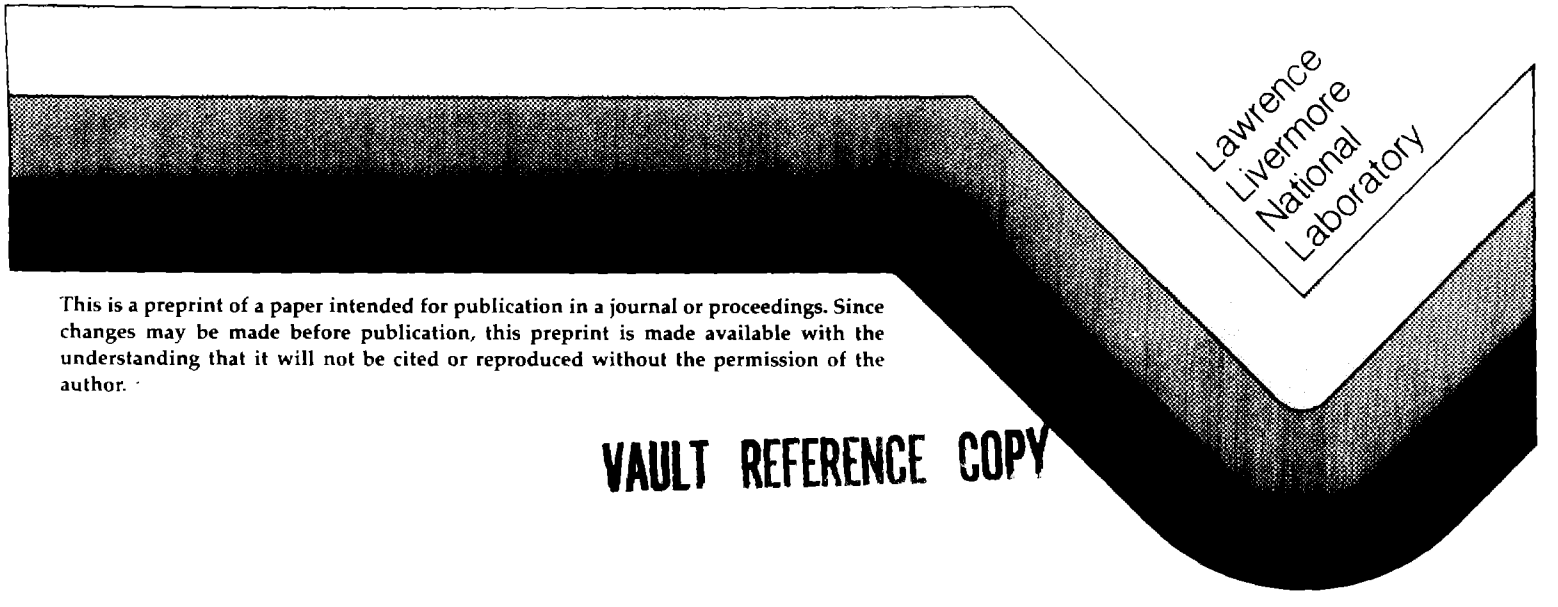

CETYLPYRIDINIUM CHLORIDE - A VERSATILE REAGENT FOR PRECIPITATION TITRATIONS

For the study of potentiometric titrations only very simple equipment is required: a pH/millivolt meter, a reference electrode, and a home-made plastic-coated graphite indicating electrode (1). Quaternary ammonium halides were found very suitable as titrants for precipitation titrations (2). We recommend cetylpyridinium chloride (CPC), a compound which is relatively non-toxic, inexpensive, and very versatile. It can be used for the determination of many inorganic and organic anions. Many cations can be determined after conversion to their halide or cyanide complexes.

BACKGROUND

Willard and Smith (3) recommended tetraphenylarsonium chloride (ϕ_4AsCl) for the gravimetric determination of some large anions and some complex halides. In 1968 Baczuk and DuBois (4) used ϕ_4AsCl for the potentiometric titration of perchlorate, using a perchlorate ion-selective electrode (ISE). We have found that quaternary ammonium halides can replace ϕ_4AsCl as the titrant in this and many other titrations (5). In earlier work we used cetyltrimethylammonium bromide as titrant (6). Recent work has shown that CPC is preferable because of its higher solubility in water, which makes it possible to use more concentrated titrant solutions(2). We have also replaced the fairly expensive commercial ISE's with inexpensive home-made plastic-coated graphite indicating electrodes (1).

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EXPERIMENTAL

The preparation of the polyinyl(chloride)/dioctylphthalate-coated graphite rod was described previously in this Journal (1). The titrant was an aqueous solution of cetylpyridinium chloride which is available from various suppliers.[1] It was prepared by dissolving 3.58 g of the monohydrate in approximately 250 ml of warm water, and diluting to volume with cold distilled water.

The experimental conditions such as feasible pH ranges, sample titration curves, and statistics of recoveries have been described in a review of the analytical applications of quaternary ammonium halides (2) and some recent work (7,8).

A few conditioning runs should preceed each experiment. This is also good practice when working with ISE's. In highly acidic solutions the coated graphite indicating electrode will deteriorate more quickly than in other media. This requires re-coating of the graphite sensor as outlined in reference (1).

INORGANIC ANIONS

A list of inorganic anions that can be determined with CPC is given in Table 1. Many anions can be titrated, with the exception of those of the elements of groups 1A through VA and group VIII. Cations in group VIIIA can easily be converted to their halides by adding an excess of potassium bromide or chloride in acid solutions. A large number of complex cyanides can

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[1]Aldrich catalog no. 85,556-1, Alfa catalog no. 13,651; Eastman catalog no. P5361. The reagent from Alfa was the least expensive material. One liter of a 0.01 M solution costs $0.17.

similarly be determined, some in acid solutions because of their great stability. A typical reaction, for the determinination of Pt^{4+}, is given by the equation. In many cases the bromide complex will yield sharper titration

$$2C_{21}H_{38}N^{+} + PtC_6^{2-} \longrightarrow (C_{21}H_{38}N)_2PtCl_6$$

curves than the corresponding chloride because of the lower solubility of the resulting cetylpyridinium precipitate.

Table 1 is not complete and many other applications are no doubt possible. Determinations of the stoichiometry of some of these reactions yielded rather unexpected results. For instance, the titration of Bi^{3+} in acid solution in the presence of excess bromide required 1.5 mole of CPC per Bi^{3+}. The composition of the resulting precipitate conformed, according to elemental analysis, to the formula $(C_{21}H_{38}N)_3Bi_2Br_7$) (8).
Molybdates and tungstates form isopoly compounds which are quite sensitive to pH and yield complex compounds in the titration.(9)

ORGANIC ANIONS

A list of organic anions that were titratable vs CPC is presented in Table 2. Only water-soluble compounds can be determined because nonaqueous, or partially nonaqueous media will dissolve the organic coating of the graphite indicating electrode. However, many alkali metal salts of organic acids and dyes are water soluble and thus can be determined. It should be noted that a minimum of 10 carbon atoms is required in the analyte for the successful titration of soaps and anionic detergents.

CONCLUDING REMARKS

We have shown numerous applications of quaternary ammonium halides for the determination of inorganic and organic anions. It is left up to the ingenuity of the student to investigate additional anions and to devise possible separations. Thus:

1. Tl^{3+} can be determined as the halide in the presence of Tl^{+}.
2. Te^{4+} can be determined as the halide in the presence of Te^{6+}.
3. Te^{4+} can be determined in the presence of Se.

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Table 1. Some Inorganic Anions Titratable vs CPC, Classified According to Subgroups of the Periodic Table.

VIA	VIIA	VIIIA		IB	IIB	IIIB	IVB	VB	VIB	VIIB
$Cr_2O_7^{2-}$	MnO_4^-	cyanides	halides	$AuCl_4^-$	$Zn(CN)_4^{2-}$	BF_4^-	$SnCl_2^{2-}$	PF_6^-	$S_2O_8^{2-}$	ClO_4^-
MoO_4^{2-}	ReO_4^-	$Fe(CN)_6^{3-}$	$Ru_2Cl_{10}^{4-}$	$Au(CN)_2^-$	$Hg(CN)_4^{2-}$	$TlCl_4^-$	$SnCl_4^{2-}$	AsF_6^-	$TeCl_6^{2-}$	IO_4^-
WO_4^{2-}		$Fe(CN)_6^{4-}$	$RhCl_6^{3-}$		$HgCl_4^{2-}$	$TlBr_4^-$		SbF_6^-		I^-
		$Co(CN)_6^{3-}$	$PdCl_4^{2-}$		$HgBr_4^{2-}$			$Bi_2Br_7^{3-}$		
		$Ni(CN)_4^{2-}$	$PdCl_6^{2-}$							
		$Pd(CN)_4^{2-}$	$OsCl_6^{2-}$							
		$Os(CN)_6^{4-}$	$IrCl_6^{2-}$							
		$Pt(CN)_4^{2-}$	$IrCl_6^{3-}$							
		$Pt(CN)_6^{2-}$	$PtCl_4^{2-}$							
			$PtCl_6^{2-}$							

Table 2 Organic Anions Titratable vs CPC

Nitroform
2,4-Dinitrobenzenesulfonate
2,4,5-Trichlorobenzenesulfonate
Picrate
Picrylsulfonate
Tetraphenylborate
Cyanotriphenylborate
Bromophenol blue
Bromocresol purple
Bathophenanthroline disulfonic acid (disodium salt)
<u>Anionic Surfactants and Soaps (sodium salts)</u>
Dioctylsulfosuccinate
Dodecylsulfate
Dodecylbenzenesulfonate
Dodecanesulfonic acid
Octylsulfate
Dodecanoate
Tetradecanoate
Stearate
Oleate